PERMEABILITIES OF COLLOIDAL SUBSTANCES TO GASES.

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It is a well known fact that almost all amorphous substances, especially colloidal substances, absorb various gases, but the mechanism is not yet clear. The India rubber, for example, is permeable to various gases(1). In the present experiment it has been examined whether other colloidal substances are also permeable for gases or not, and hence whether their sorption is an adsorption phenomenon or not. The author wishes, also, to discuss on the mechanism of the permeability and absorption.

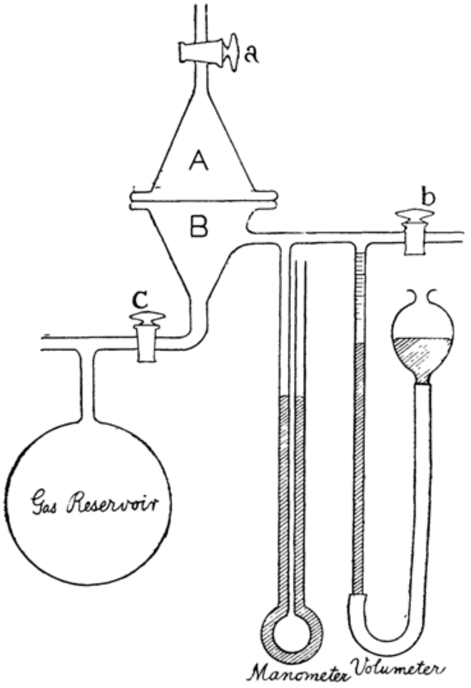

Fig. 1.

Experimentals. The apparatus used in this experiment is shown in Fig. 1. The membrane of the colloidal substance to be examined is placed between A and B. The stop-cocks a and b are opened and the air exist in the vessel and some gases which may be sorped in the mass of the membrane are exhausted by a pump. Then the cocks a and b are closed, and the gas under examination is introduced into B through the cock c. The volume change of the gas is measured with a volumeter.

The membranes used were of rubber, celluloid and geletine, while the gas tested were hydrogen, oxygen, carbon dioxide, sulphur dioxide and ammonia. For the first several hours, before the stationary state is reached, the effect of absorption is very large. The data shown in the following tables were obtained.

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(1) Graham, *J. Chem. Soc.*, 20 (1867), 235; Wroblewski, *Ann. Physik*, 8 (1879), 29; Hüfner, *Ann. Phys. u. Chem.*, 34 (1886), 1; Edwards and Pickering, *Chem. Met. Eng.*, 23 (1920), 17; Daynes, *Proc. Roy. Soc.* (*London*), 97 A (1920), 286; Venable and Fuwa, *Ind. Eng. Chem.*, 14 (1922), 139.

TABLE 1.

Celluloid.

Oxygen		Hydrogen		Carbon dioxide		Ammonia	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
5	0.32	10	0.40	9	1.14	8	9.46
10	0.48	20	0.72	19	1.90	16	16.45
20	0.68	30	0.92	29	2.52	26	22.80
30	0.80	40	1.26	59	3.72	38	28.25
50	1.20	60	1.72	99	5.18	44	36.97
81	1.34	90	2.39	119	5.64	65	41.37
120	1.67	120	3.10	149	6.57	90	47.62
180	1.97	180	4.36	179	7.43	120	57.61
251	2.40	240	5.74	239	9.24	150	69.07
307	2.47	300	7.18	310	11.37	180	75.10
371	2.70	365	8.40	370	13.11	233	92.00
428	2.86	420	9.57	430	14.80	290	104.91
480	3.06					345	115.37
						413	129.34

These data are depicted in Fig. 2.

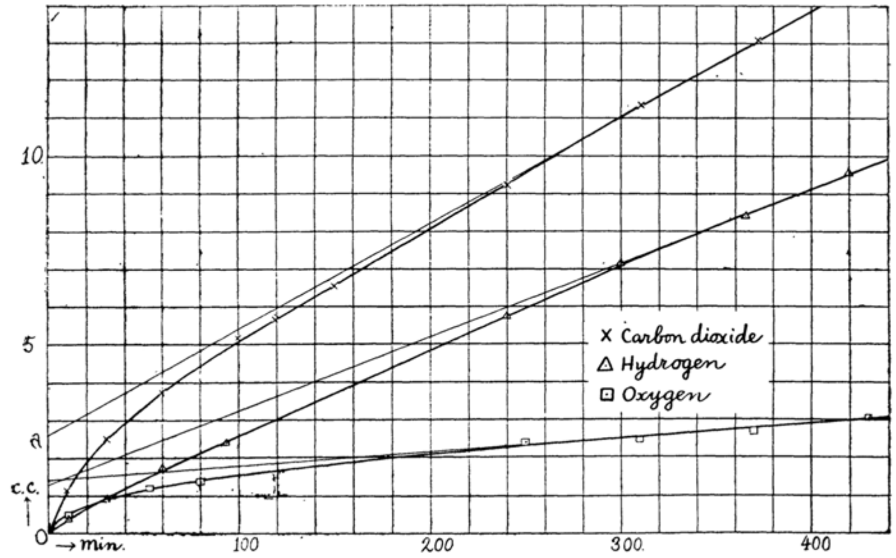

Fig. 2.

Table 2.

Rubber.

Oxygen		Hydrogen		Carbon dioxide		Sulphur dioxide		Ammonia	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
10	0.04	5	0.133	5	0.58	13	18.57	8	10.83
20	0.05	10	0.185	10	0.86	22	26.50	17	19.46
50	0.17	20	0.230	20	1.357	32	33.59	28	27.32
110	0.33	30	0.285	31	1.76	42	37.78	40	35.59
240	0.78	40	0.385	40	2.16	50	43.40	48	40.02
300	0.91	50	0.44	50	2.49	60	47.36	58	45.77
367	0.99	60	0.472	60	2.80	90	57.63	90	61.54
436	1.08	90	0.617	90	3.57	120	65.56	150	88.36
1372	2.95	120	0.887	120	4.29	180	78.03	200	106.34
		180	1.219	180	5.66	240	88.43	310	137.50
		240	1.503	240	6.633	300	97.00	410	165.43
		300	1.875	300	7.954	360	105.97	530	192.34
				423	10.23	422	114.45		

(The measurements on the ammonia and the sulphur dioxide have been suspended after the time shown in the bottom line of the table until the stationary state was reached.)

Table 3.

Gelatine.

Oxygen		Carbon dioxide		Sulphur dioxide	
Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.	Time min.	Volume change (N.T.P.) c.c.
5	0.06	5	0.058	10	0.55
10	0.11	10	0.162	20	1.09
21	0.16	20	0.235	30	1.35
30	0.19	30	0.254	40	1.62
40	0.22	60	0.402	50	1.90
50	0.30	120	0.556	55	1.98
60	0.36	180	0.664	85	2.58
133	0.43	240	0.78	175	3.68
421	0.64	360	0.79	235	4.28
1375	0.815	450	0.85	295	4.82
		1410	1.328	355	5.24
				445	5.82

(The measurement on the ammonia was done only after the stationary state was reached.)

We must, therefore, continue the experiment until the volume change becomes constant, and then determine the permeability by dividing the volume change by the time interval. The relative permeabilities to the various gases are shown in the following table. (in the case of rubber, permeability to hydrogen has been taken as unity; but in other cases, oxygen as unity.)

TABLE 4.

Membrane / Gas	Celluloid	Rubber	Gelatine	Viscosity coeff. of gas at 20°C.	Square root of gas density
Hydrogen	2.60	1.00	less than 1.00	930×10^{-7}	1.41
Oxygen	1.00	0.35	1.00	2120×10^{-7}	5.66
Carbon dioxide	8.76	3.17	4.13	1600×10^{-7}	6.63
Sulphur dioxide	—	7.90	31.90	1380×10^{-7}	8.00
Ammonia	62.3	11.4	95.2	1080×10^{-7}	4.12

Theoretical Considerations. As it became clear that these substances are permeable to gases, there is no doubt that the sorption of various colloidal substances is not an adsorption phenomenon, that is condensation of the gaseous molecules on the surface of the substance only. It will, then, be discussed something about the mechanism of the absorption judging from the present experiments. For the passability of the gas through the membrane two causes can be considered, namely the passing of gas through the pores of the substance and the dissolution.

Pass through the Pores of the Membrane. As for the porosity of the colloidal substance many authors have discussed for long time. If we assume the permeability is due to the porosity, we have to consider two cases, namely, the viscosity flow and the molecular flow.

In the case of the viscosity flow, the rate of permeabilities for various gases will be inversely proportional to the viscosities of gases, as shown in the following well known equation.

$$q = \frac{\pi r^4 (p_0 - p) t}{8 \eta l}$$

where q denotes the mass of the gas which pass through the unit area of the membrane and η, the viscosity coefficient of the gas. The viscosity coefficients of the gases are shown in the 5th column of Table 4.(1) Thus ammonia is more viscous than hydrogen, while the former is far more passable through membranes than the latter. It is known, therefore, that the viscosity flow is not the main cause of the permeability.

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(1) Landolt-Börnstein, "Physikalisch-chemische Tabellen", 5 ed.

If the radius of pores is very small and the mean free path of the molecules is not negligible compared with the radius of pores it is the case of the molecular flow, and the permeability is inversely proportional to the square root of the density of gas.(1) But such a relation does not exist as shown in Table 4.

Dissolution. As has been discussed above, it is not quite plausible to assume that the permeability is due to the porosity. I think it is due to the solubilities of the gases into the membranes, and this idea is supported by many other facts. For example, the order of the solubilities of gases in these substances are almost the same as those in other substances like water. The gases of lower polarity is dissolved less while those of higher dissolved much. By the aid of the Fick's law the dissolution theory can also explain the fact that the orders of permeabilities are inverse to those of absorption in some cases.

From the Fick's law,

$$\frac{dq}{dt} = -D\ \frac{dy}{dx}$$

where y denotes the concentration at x, we have the following equation by using the Fourier's expansion,

$$y = y_1 + (y_2 - y_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{n=\infty} \frac{y_2 \cos n\pi - y_1}{n}\ \sin\frac{n\pi}{l}\,x .\, e^{-Dn^2\pi^2 t/l^2}$$

In the present experiment,

$$y_1 = 0 \quad at \quad x = 0.$$

By the Henry's law we have the following condition,

$$y_2 = Ap \quad at \quad x = l$$

where A is the absorption coefficient.
We obtain, therefore,

$$q = \frac{DAp}{l}\left[t + 2\sum_{n=1}^{n=\infty} \frac{l^2}{D\,n^2\pi^2}\,(1 - e^{-Dn^2\pi^2 t/l^2})\right]$$

and when t is large this equation takes the form,

$$q \because \frac{DAp}{l}\left(t + \frac{l^2}{3D}\right)$$

In this equation the first term $DApt/l$ is the quantity of the gas which passes through the membrane after the stationary state has been reached. From this it can be understood that the permeability is related to both the

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(1) Loeb, "Kinetic theory of gases", p. 252.

absorption coefficient (A) and the diffusion coefficient (D). Therefore, if D is very large or very small compared with A, the orders of the permeabilities are not the same as those of the absorption. The second term $Ap\,l/3$ corresponds to Oa in Fig. 2.

From the present experiments it cannot be judged whether the dissolution is a purely physical phenomenon or the chemical changes occur at the same time. But, in the case of the rubber it has been shown by Edwards and Pickering(1) that the solubility of sulphur dioxide is greater than that of ammonia. On the contrary, in the ordinary solvent, the solubility of ammonia is greater than that of sulphur dioxide. It is probable that there occurs some chemical change in this case. In the case of ammonia through celluloid, after putting the membrane in the atmosphere of ammonia for a long time, the permeability increased as much as five times in comparison with the data shown in Table 4—0.2056 c.c. per min. in the experiment from which Table 4 was obtained, while 1.110 c.c. per min. after putting it in the atmosphere of ammonia for about four days—and the colour changed from white to yellow and increased transparency. Such effects also might be due to the chemical change. I think that it may be due to the chemical change in the most cases where the ammonia is dissolved much in solvent.

Summary.

1. Permeabilities of rubber, gelatine and celluloid for oxygen, hydrogen, carbon dioxide, sulphur dioxide, and ammonia were determined.

2. By ascertaining the permeabilities of celluloid and gelatine, it became clear that the sorptions of these substances are not adsorption phenomena.

3. Something about the mechanism of permeability and absorption was discussed and the author reached the conclusion that the permeability and hence the absorption is caused by the dissolution of gas in the colloidal substance.

In conclusion I wish to express my sincere thanks to Prof. J. Sameshima for his kind guidance during this experiment.

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(1) Loc. cit.